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Liquid−Liquid Equilibria for the Ternary System Water + Octane + Diethylene Glycol Monobutyl Ether

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In this work, we present the liquid−liquid equilibrium data of a ternary system, water + octane + diethylene glycol monobutyl ether, at 283.15 K, 293.15 K, and 303.15 K under atmospheric pressure. The experimental data were correlated with the UNIQUAC model, and a good agreement was obtained.

Introduction

Ternary systems of the type water + oil + surfactant have been investigated extensively because of their wide applications in industrial processes, such as herbicides, tertiary oil recovery, and liquid−liquid extraction processes.[1,2] Nonionic surfactants of the homologous series of alkylpoly(glycol ethers) $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$, abbreviated by C_iE_j hereafter, are widely used as detergents by means of forming stable homogeneous solutions with high fractions of water and oil, the so-called “microemulsions”.[3,4] The phase behavior of the mixtures of the type water + oil + nonionic surfactant also plays an important role in the research of critical phenomena[5] and wetting transitions.[6−8] In our laboratory, we have investigated the phase behavior of water + C_iE_j binary systems[9] and two ternary systems, water + dodecane + C_6E_2[10] and water + tetradecane + C_6E_2.[11] In this work, we present liquid−liquid equilibrium measurements of the ternary system water + octane + C_4E_2 at 283.15 K, 293.15 K, and 303.15 K under atmospheric pressure. The experimental equilibrium data were further correlated with the UNIQUAC model. The phase behavior of the ternary system was successfully described by the UNIQUAC model.

Experimental Section

Octane was purchased from Merck with a purity of 99%. The nonionic surfactant diethylene glycol monobutyl ether (C_4E_2) was an Aldrich Chemical product with a purity of 99%. These two chemicals were used as received. Water was purified by a Millipore Milli-RO PLUS 10 and Milli-Q system with a resistivity of >18.2 MΩ·cm.

To analyze the composition of the samples, a gas chromatograph (China Chromatography 9800) equipped with a thermal conductivity detector was used. The stainless steel chromatographic column (Poropak P 80/100 mesh) was 2 m length × 3.175 mm diameter. The signal was transferred to an integrator (Shimadzu, Chromatopac C-R6A) to accomplish data recording. The injection-port temperature was fixed at 543.15 K, while the detector temperature was held at 573.15 K. The oven temperature was initially held at 468.15 K and then raised to a final temperature of 513.15 K at a speed of 10 K·min^{-1} 2 min after each injection. The flow rate of the carrier gas, helium, was kept at 60 mL·min^{-1}. Single-phase binary mixtures of water + C_4E_2 and octane + C_4E_2 with known compositions were used to calibrate the gas chromatograph in the composition range of interest. Each composition was analyzed at least three times.

Table 1. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Octane (2) + C_4E_2 (3) at 283.15 K

experimental results				calculated results			
w_1^u	w_3^u	w_1^l	w_3^l	w_1^u	w_3^u	w_1^l	w_3^l
0.0001	0.0138	0.8257	0.1743	0.000 02	0.0020	0.8196	0.1798
0.0001	0.0165	0.7463	0.2523	0.000 05	0.0033	0.7410	0.2577
0.0002	0.0176	0.6715	0.3252	0.000 08	0.0049	0.6678	0.3299
0.0002	0.0186	0.6062	0.3878	0.000 11	0.0067	0.6027	0.3935
0.0002	0.0203	0.5228	0.4661	0.000 18	0.0094	0.5260	0.4669
0.0002	0.0212	0.4528	0.5288	0.000 27	0.0129	0.4544	0.5330
0.0003	0.0219	0.4038	0.5714	0.000 37	0.0164	0.3993	0.5811
0.0003	0.0240	0.3260	0.6360	0.000 55	0.0222	0.3292	0.6367
0.0004	0.0282	0.2646	0.6797	0.000 79	0.0298	0.2643	0.6790
0.0004	0.0324	0.2294	0.7000	0.000 97	0.0355	0.2277	0.6968
0.0006	0.0372	0.1905	0.7174	0.001 19	0.0433	0.1872	0.7091
0.0008	0.0455	0.1464	0.7277	0.001 66	0.0567	0.1428	0.7103
0.0019	0.0706	0.0962	0.7049	0.002 17	0.0789	0.0947	0.6906
0.0045	0.1146	0.0682	0.6513	0.003 49	0.1094	0.0690	0.6566
average absolute deviation				0.000 3	0.0080	0.0030	0.0061

For each tie line, three sealed test tubes with the same total composition as that of the water + octane + C_4E_2 mixture were prepared. The vapor−liquid ratio in the tubes was about 1. These samples were vigorously shaken and then placed in a water thermostat for at least 24 h to reach equilibrium. The temperature stability of the water thermostat was ±0.05 K. During the equilibration process, these samples were shaken several times to ensure thorough mixing. After equilibrium was reached, both liquid phases were analyzed by the gas chromatograph to determine the compositions. The compositions of water, octane, and C_4E_2 in each phase were determined by averaging over the three samples with the same total composition for each tie line. The experimental uncertainty was within ±0.0009 mass fraction.

In the oil-rich (upper) phase, the Karl Fischer titration method (MKC-210, Kyoto Electronics Co., Japan) was used to analyze the water composition, because the water trace was not resolvable by the gas chromatograph.

Results and Discussion

The experimental compositions of the equilibrium phases of the ternary system water + octane + C_4E_2 at 283.15 K, 293.15 K, and 303.15 K are listed in Tables 1−3. The data are expressed in units of mass fraction *w*. The superscripts

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Table 2. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Octane (2) + C_4E_2 (3) at 293.15 K

experimental results				calculated results			
w_1^u	w_3^u	w_1^l	w_3^l	w_1^u	w_3^u	w_1^l	w_3^l
0.0002	0.0200	0.8316	0.1684	0.0001	0.0078	0.8232	0.1758
0.0003	0.0221	0.7472	0.2509	0.0002	0.0106	0.7440	0.2542
0.0003	0.0230	0.6733	0.3223	0.0002	0.0129	0.6713	0.3255
0.0003	0.0244	0.6059	0.3862	0.0003	0.0149	0.6068	0.3879
0.0003	0.0269	0.5249	0.4613	0.0004	0.0174	0.5281	0.4625
0.0004	0.0273	0.4505	0.5278	0.0004	0.0201	0.4554	0.5285
0.0004	0.0296	0.3934	0.5768	0.0005	0.0226	0.3992	0.5763
0.0005	0.0335	0.3219	0.6337	0.0006	0.0265	0.3277	0.6309
0.0006	0.0370	0.2638	0.6723	0.0008	0.0317	0.2616	0.6717
0.0007	0.0414	0.2287	0.6922	0.0009	0.0357	0.2246	0.6883
0.0009	0.0474	0.1882	0.7101	0.0011	0.0416	0.1839	0.6994
0.0015	0.0594	0.1455	0.7138	0.0014	0.0513	0.1396	0.6994
0.0036	0.0948	0.0944	0.6755	0.0019	0.0699	0.0916	0.6775
0.0100	0.1765	0.0618	0.5915	0.0023	0.0872	0.0668	0.6509
average absolute deviation				0.0008	0.0152	0.0042	0.0080

Table 3. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Octane (2) + C_4E_2 (3) at 303.15 K

experimental results				calculated results			
w_1^u	w_3^u	w_1^l	w_3^l	w_1^u	w_3^u	w_1^l	w_3^l
0.0004	0.0283	0.8363	0.1629	0.0001	0.0051	0.8215	0.1776
0.0004	0.0310	0.7545	0.2430	0.0001	0.0075	0.7430	0.2553
0.0004	0.0322	0.6776	0.3165	0.0002	0.0098	0.6700	0.3270
0.0004	0.0336	0.6155	0.3747	0.0002	0.0121	0.6058	0.3893
0.0005	0.0344	0.5323	0.4502	0.0003	0.0153	0.5276	0.4633
0.0005	0.0364	0.4555	0.5197	0.0004	0.0188	0.4558	0.5286
0.0005	0.0392	0.4014	0.5649	0.0005	0.0221	0.4010	0.5753
0.0006	0.0434	0.3290	0.6217	0.0007	0.0277	0.3287	0.6304
0.0007	0.0483	0.2637	0.6652	0.0009	0.0348	0.2624	0.6705
0.0008	0.0539	0.2278	0.6833	0.0011	0.0400	0.2252	0.6864
0.0012	0.0611	0.1889	0.6972	0.0014	0.0477	0.1845	0.6958
0.0019	0.0752	0.1444	0.6972	0.0018	0.0603	0.1397	0.6928
0.0065	0.1370	0.0911	0.6459	0.0026	0.0835	0.0913	0.6636
average absolute deviation				0.0005	0.0207	0.0048	0.0096

u and l stand for the upper and lower liquid phases, respectively. For the condition of very low water contents in the octane-rich phase, the Karl Fischer titration method was applied to determine the water content. Note that the mass fractions of water in the octane-rich phase are generally lower than the experimental uncertainty of the gas chromatograph. Figures 1−3 show the corresponding triangular phase diagrams. Total compositions of samples prepared for tie-line measurements are given in Figures 1−3 by solid diamonds. The fit of a linear expression to each tie line and its corresponding total composition data point is always better than 0.999. Note that, in the temperature range of our experiments, the two-phase region slightly shrinks with increasing temperature, and there is no three-phase-coexisting region, consistent with the observation of Kahlweit et al.[13]

Mainly, the surfactant C_4E_2 partitions into an aqueous phase, as shown in Figures 1−3. The composition of C_4E_2 is relatively small in the upper oil-rich phase. Kilpatrick et al.[14] also pointed out that the partitioning of C_4E_2 between aqueous and oil-rich phases is fairly insensitive to the alkane chain length. In addition, the two-phase region of the mixture water + C_4E_2 + alkane slightly enlarges along with an increase of the oil chain length.[14]

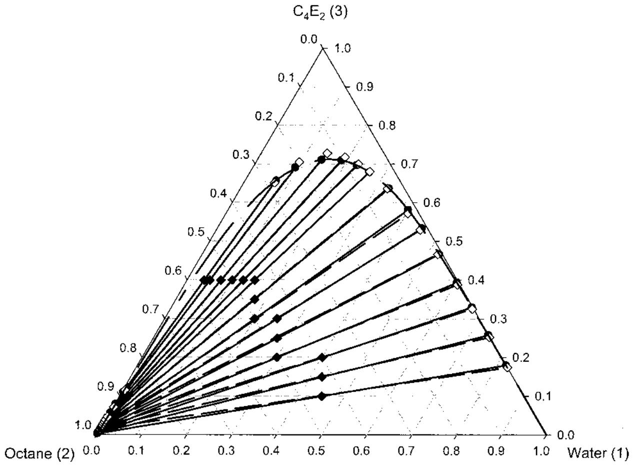

Figure 1. Ternary liquid−liquid equilibria (mass fraction) for the system water (1) + octane (2) + C_4E_2 (3) at 283.15 K: experimental tie lines (◇, dashed line), calculated tie lines (●, solid line), calculated binodal curve (long dashed curve), and experimental total compositions (◆).

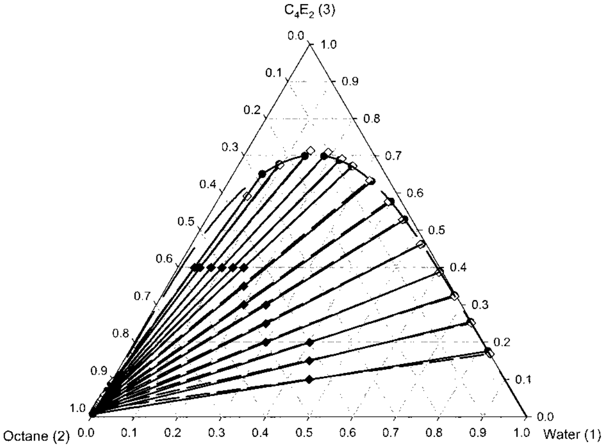

Figure 2. Ternary liquid−liquid equilibria (mass fraction) for the system water (1) + octane (2) + C_4E_2 (3) at 293.15 K: experimental tie lines (◇, dashed line), calculated tie lines (●, solid line), calculated binodal curve (long dashed curve), and experimental total compositions (◆).

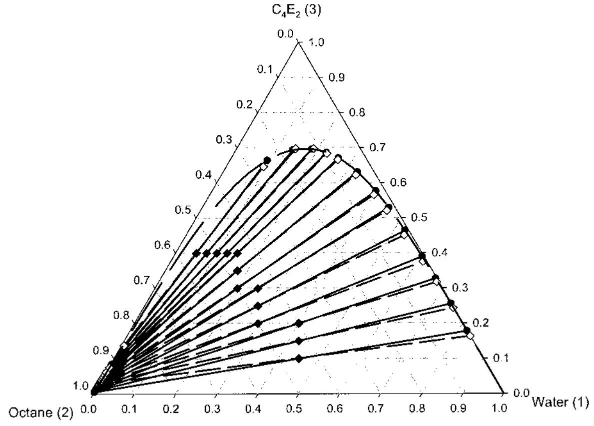

Figure 3. Ternary liquid−liquid equilibria (mass fraction) for the system water (1) + octane (2) + C_4E_2 (3) at 303.15 K: experimental tie lines (◇, dashed line), calculated tie lines (●, solid line), calculated binodal curve (long dashed curve), and experimental total compositions (◆).

The UNIQUAC model of Abrams and Prausnitz[12] was used to correlate the experimental data. In this work, the relative van der Waals volume r_i and van der Waals surface area q_i were adopted from the UNIFAC group contribution of Hansen et al.,[15] listed in Table 4. The effective binary interaction parameter, a_{ij},[16] is defined by

$$u_{ij} - u_{jj} = a_{ij}R \qquad (1)$$

Table 4. Relative van der Waals Volume *r* and van der Waals Surface Area *q*[15]

compound	*r*	*q*	compound	*r*	*q*
water	0.9200	1.4000	C_4E_2	6.1695	5.0760
n-octane	5.8486	7.1974			

Table 5. UNIQUAC Effective Binary Interaction Parameters[16] for the System Water (1) + Octane (2) + C_4E_2 (3)

	283.15 K		293.15 K		303.15 K	
ij	a_{ij}/K	a_{ji}/K	a_{ij}/K	a_{ji}/K	a_{ij}/K	a_{ji}/K
12	224.39	2457.46	195.95	2446.88	211.70	2501.32
13	125.19	−197.74	122.81	−138.66	123.97	−168.17
23	231.86	−90.11	258.67	−100.06	258.83	−104.86

where R is the gas constant and u_{ij} is the UNIQUAC interaction parameter between molecules i and j.

There are two effective binary interaction parameters for a pair of substances, and thus six effective binary interaction parameters are required for a ternary system. In this work, these six effective binary interaction parameters were determined by numerically minimizing the following objective function.[17]

$$F_x = \sum_k \sum_{j=1}^{2} \sum_{i=1}^{3} W_{ijk}(x_{ijk}^{\text{expl}} - x_{ijk}^{\text{calc}})^2 \qquad (2)$$

where x_{ijk}^{expl} and x_{ijk}^{calc} are the experimental and calculated mole fractions of component i in phase j along a tie line k, respectively. The symbol W_{ijk} is the weight factor, whose value is defined as the reciprocal of the square of x_{ijk}^{expl}. The liquid−liquid equilibrium flash calculation[18] was applied to evaluate the compositions of both liquid phases along each tie line by using the experimental total compositions as input data. The minimization of the objective function F_x was accomplished by using the subroutine DUMPOL of the IMSL library.[19]

The regression results of the UNIQUAC effective binary interaction parameters are shown in Table 5. Note that these parameters are temperature-dependent. The regression results for each tie line are given in Tables 1−3 to make a comparison with experimental data. The average absolute deviations between experimental data and calculated results are small and also listed in the bottom of Tables 1−3. The regression results are good, and the deviation slightly increases upon approaching a plait point, as shown in Figures 1−3. The calculated binodal curves are also presented by long dashed curves in Figures 1−3. As one can see, the phase behavior of the system water + octane + C_4E_2 is successfully described by the UNIQUAC model.

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